Thermal stability of titanium nitride for shallow junction solar cell contacts

N. W. Cheung, [a] H. von Seefeld, and M-A. Nicolet
California Institute of Technology, Pasadena, California 91125

F. Ho and P. Iles
Applied Solar Energy Corporation, City of Industry, California 91746

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To demonstrate the thermal stability of titanium nitride as a high-temperature diffusion barrier, the TiN-Ti-Ag metallization scheme has been tested on shallow-junction (~ 2000 Å) Si solar cells. Electrical measurements on reference samples with the Ti-Ag metallization scheme show serious degradation after a 600 °C, 10-min annealing. With the TiN-Ti-Ag scheme, no degradation of cell performance is observed after the same heat treatment if the TiN layer is $\gtrsim 1700$ Å. The glass encapsulation of cells by electrostatic bonding requires such a heat treatment.

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Reliable metallic contacts to solar cells have been a subject of interest to the photovoltaic industry. Frequently, the failure or degradation of cell performance is caused by the deterioration of electrical contacts near the *p-n* junction during processing steps involving high-temperature thermal treatments. For example, modern packaging processes of solar cells intended for outer-space usage may require an electrostatic bonding step to replace the adhesive presently used to attach thin glass covers to the cell. These covers are about 150 μm thick and protect the cell from damage by energetic particles (primarily protons in the 100-keV range) and also increase the emissivity of the cell in the infrared, thereby reducing the operating temperature of the cell. In the electrostatic bonding process, the metallization scheme is subjected to heat treatment of 600 °C for 10 min. At such elevated temperatures, atomic interdiffusion takes place across the metal-semiconductor interface and the presence of metallic impurities near the *p-n* junction can degrade the photovoltaic conversion mechanisms by forming recombination centers. In some severe cases, penetration of the metal through the *p-n* junction can even short out the junction completely. These problems are particularly pertinent to shallow-junction solar cells (~ 2000 Å) which are often preferred for their high current efficiency.

To alleviate the interdiffusion problem, it seems promising to apply the concept of diffusion barriers[1] to solar cell metalization schemes. The idea is to interpose material "*X*," the diffusion barrier, between layers *A* and *B*, so that the undesirable thermal diffusion is suppressed while the electrical and mechanical properties of the *A-X-B* structure remain unaltered or at least equivalent to the *A-B* metal combination. An important aspect of the diffusion barrier concept is to free the designer from various metallurgical constraints. Since the choice of metals is generally dictated by metallurgical and processing considerations, the application of an appropriate diffusion barrier may provide more variety to the selection of materials.

As a choice for the diffusion barrier material, we have singled out titanium nitride (TiN) because of its low electrical resistivity and high chemical stability. Metallurgical studies on the diffusion barrier properties of TiN have been reported by Wittmer[2] on metal-metal couples and by Cheung *et al.*[3] on metal-silicon systems. Fournier[4] has applied a layer of TiN between Ti and Pt layers in the metallization scheme for insulated-gete field-effect transistors. His results demonstrate that the diffusion of Pt into Ti is blocked effectively during a heat treatment of 30 min at 450 °C. In the Au-Pt-Ti scheme for beam-lead devices, Garceau *et al.*[5] have also reported that the incorporation of a 100-Å-thick TiN layer between Ti and Pt can inhibit the formation of the intermetallic TiPt. In the present study, we have demonstrated the thermal stability of TiN as a diffusion barrier up to 600 °C for shallow-junction (~ 2000 Å) Si solar cell contacts.

The 2 cm $\times$ 2 cm n^+-on-*p* Si solar cells with a junction depth of ~ 2000 Å were provided by Applied Solar Energy Corporation. The n^+ layer is phosphorus doped. The boron-doped *p*-type substrates (~ 10 mil thick) are from Czochralski-pulled Si crystals and are coated with 4 μm of Ag as the back contact. In this feasibility study, the special metallization pattern on the cells consists of parallel fingers about 1 mm wide and ~ 1 mm apart. Mechanical masking procedures were used to define the patterns during TiN deposition and metal evaporation.

The TiN thin films were prepared in a rf sputtering deposition chamber equipped with 7.5-cm diameter, planar magnetron sputtering targets (pure Ti). A sputtering rf power of 1 kW and nitrogen pressure of 70 mT were used for the reactive sputtering of TiN, with typical deposition rates of ~ 100 Å per minute. Different TiN thicknesses were obtained by varying the deposition times. The electrical resistivity of the TiN layers was on the order of 500 $\mu\Omega$ cm. Although lower resistivities can be obtained by higher sputtering powers and lower nitrogen pressures, [6] it has been observed that the adhesion of TiN to silicon is satisfactory only at higher nitrogen pressures. Despite the higher bulk resistivity of TiN (approximately a factor of 4 higher than that of evaporated Ti films), the TiN-Ti-Ag system has an *I-V* performance comparable with the Ti-Pd-Ag metalliza-

[a] Present address: Department of Electrical Engineering and Computer Sciences, University of California, Berkeley, California 94720.

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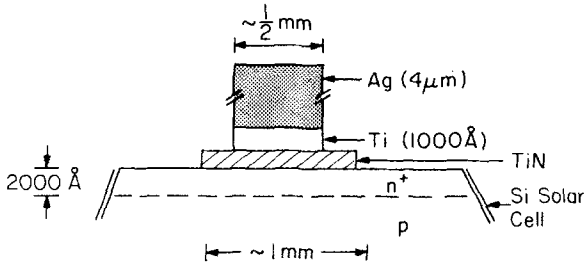

FIG. 1. Schematic of the TiN-Ti-Ag metallization system on a Si solar cell.

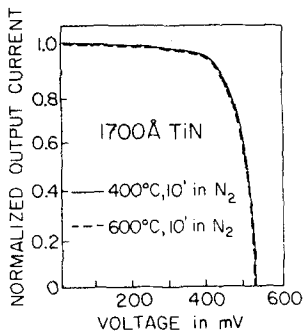

FIG. 3. *I-V* characteristic of a shallow-junction (~2000 Å) Si solar cell with the TiN-Ti-Ag metallization scheme before (solid line) and after (dotted line), a 600 °C, 10 min annealing. The TiN layer is ~1700 Å thick. The *I-V* curves are measured with AMO illumination.

tion scheme when tested on the n^+-*on*-*p* solar cells. This is because the effective series resistance R_s of the cell is dominated by contact resistance across the metal-Si interface and series resistance along the metallic stripes. With a 4-μm-thick and 1-cm-long Ag layer as the major electrical conductor, the resistance across the TiN thickness (1000–2000 Å) will contribute negligibly to R_s.

The schematic of the metallization layers is shown in Fig. 1. After the TiN layer deposition (500 to 2000 Å in thickness), a thin Ti layer (~1000 Å) was evaporated on top of TiN in a separate evaporation chamber followed by a 4-μm-thick Ag layer. The Ti layer was used to improve the adhesion between Ag and TiN. To avoid mask registration problems, the Ti and Ag stripes were made only ½ mm wide so that they would not overlap the edges of the TiN layer.

The 600 °C annealing was performed under manufacturing conditions with a flowing nitrogen ambient. No particular attention was paid to the dryness of the nitrogen gas or the presence of oxygen in the annealing ambient. Prior to the 600 °C, 10-min heat treatment, all the cells were sintered at 400 °C for 10 min to minimize the contact resistance between the metallization and Si.

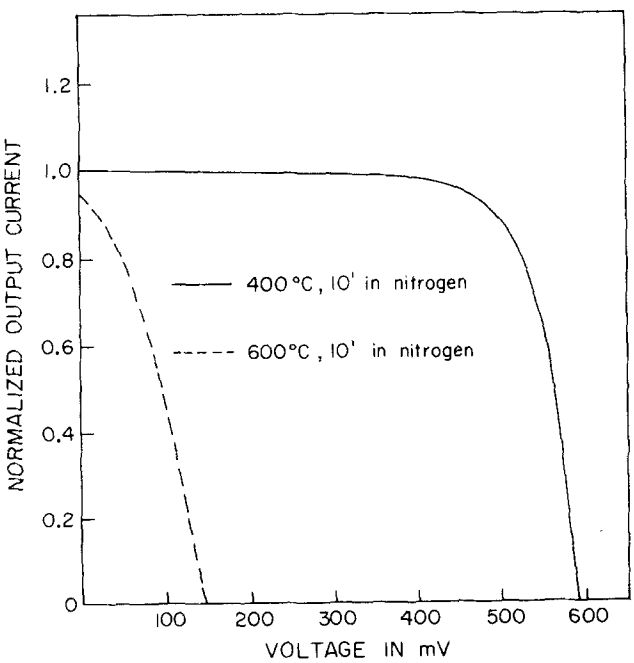

FIG. 2. *I-V* characteristic of a shallow-junction (~2000 Å) Si solar cell with the Ti-Ag metallization scheme under AMO illumination. The solid line denotes the cell's performance after a 400 °C, 10 min annealing. The dashed line shows the degradation after a 600 °C, 10-min heat treatment.

For comparison, reference samples without the TiN layer (i.e., the Ti-Ag metallization scheme) were also prepared and heat treated at 600 °C for 10 min. Results on the *I-V* measurements under AMO illumination are shown in Fig. 2. Both V_{oc} (open circuit voltage), I_{sc} (short circuit current) and the fill factor are observed to be significantly reduced after the thermal annealing. Following the analysis of Hovel,[7] the results indicate that the shunt resistance R_{sh} and the series resistance R_s of the junction and metallization scheme are lowered and raised, respectively. The decrease in R_{sh} reflects the fact that the *p-n* junction can either be contaminated or even short circuited locally by the presence of metallic elements. The intermixing of Si-Ti-Ag can lead to an increase in R_s because of the increase in the contact resistance with Si and/or the resistivity of the metal films by forming a ternary alloy. This observation is in good agreement with previous diffusion studies that established the thermal instability of the Si-Ti-Ag system at 600 °C.[3]

The *I-V* characteristic of solar cells with the TiN-Ti-Ag metallization scheme was also measured under AMO illumination before and after the 600 °C, 10-min annealing cycle. For TiN thicknesses between 750 and 1700 Å, no degradation of V_{oc} could be detected, which indicates that R_{sh} remains constant during the heat treatment. However, the fill factor of the *I-V* curves shows a thickness dependence on the TiN layer and decreases with decreasing TiN layers. Beyond a TiN thickness of 1700 Å, no change in V_{oc}, I_{sc}, and fill factor can be detected after the 600 °C annealing (Fig. 3). Thus, with a sufficiently thick TiN layer, the normal failure mode of Si solar cells after high-temperature heat treatments can be circumvented without sacrifice in the cells' electrical performance.

In summary, we have demonstrated that TiN films can be used as a diffusion barrier for high-temperature processing. In particular, with the TiN-Ti-Ag metallization scheme on shallow-junction (~2000 Å) Si solar cells, no degradation of cell performance is observed after a 600 °C, 10-min heat treatment if the TiN layer is $\gtrsim$ 1700 Å. In practice, a 500-Å-thick Pd layer would be sandwiched between the Ti and Ag layers to passivate the electrochemical reaction between Ti and Ag when the cells are exposed to moisture.[8]

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